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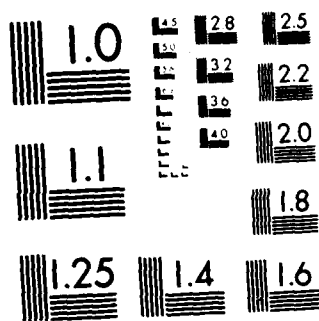
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OFFICE OF NAVAL RESEARCH

CONTRACT N00014-75-C-0880

Task No. NR 051-579

TECHNICAL REPORT NO. 40

"PHOTOCHEMICAL CONVERSION OF  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{P-Donor})$  TO  
 $\text{H}_2\text{Os}_3(\text{CO})_9(\text{P-Donor})$  IN SOLUTION AND ON HIGH SURFACE AREA SILICA"

by

James G. Bentsen and Mark S. Wrighton

Prepared for Publication

in

Inorganic Chemistry

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

December 28, 1983

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-40	2. GOVT ACCESSION NO. AD 1111771	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Photochemical Conversion of $H_2Os_3(CO)_{10}(P-Donor)$ to $H_2Os_3(CO)_9(P-Donor)$ in Solution and on High Surface Area Silica"		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) James G. Bentsen and Mark S. Wrighton		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Rm. 6-335 Massachusetts Institute of Technology Cambridge, Massachusetts 02139		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0880
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-579
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December 28, 1983
		13. NUMBER OF PAGES 18
		14. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States Government; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared and accepted for publication in <u>Inorganic Chemistry</u> .		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) photochemistry, ultra-violet irradiation, chemical conversion		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Near-UV irradiation of $H_2Os_3(CO)_{10}L$ yields conversion to the known coordinatively unsaturated $H_2Os_3(CO)_9L$ for $L = PPh_3$ or $PPh_3Et$ in alkane solution at 298 K. Likewise, near-UV irradiation of an alkane suspension of $[SiO_2]-L'O_s_3-$ $(CO)_{10}H_2$ yields $[SiO_2]-L'O_s_3(CO)_9H_2$ where $[SiO_2]-L'O_s_3(CO)_{10}H_2$ is the solid prepared by reaction of high surface area $SiO_2$ with $H_2Os_3(CO)_{10}(PPh_2CH_2CH_2Si(OEt)_3)$ . The same photochemistry results at 77 K in rigid alkane glasses, but the initial ( $<5\%$ conversion) product is not derived from loss of CO. Continued irradiation at 77 K yields $H_2Os_3(CO)_9L$ and CO, but $H_2Os_3(CO)_9L$ is only found in $\sim 50\%$ (over)		

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yield based on the amount of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  consumed. Warming the irradiated sample to 298 K yields some regeneration of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  and some additional  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$ .

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Photochemical Conversion of  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{P-Donor})$  to  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{P-Donor})$  in Solution and on High Surface Area Silica.

James G. Bentsen and Mark S. Wrighton\*

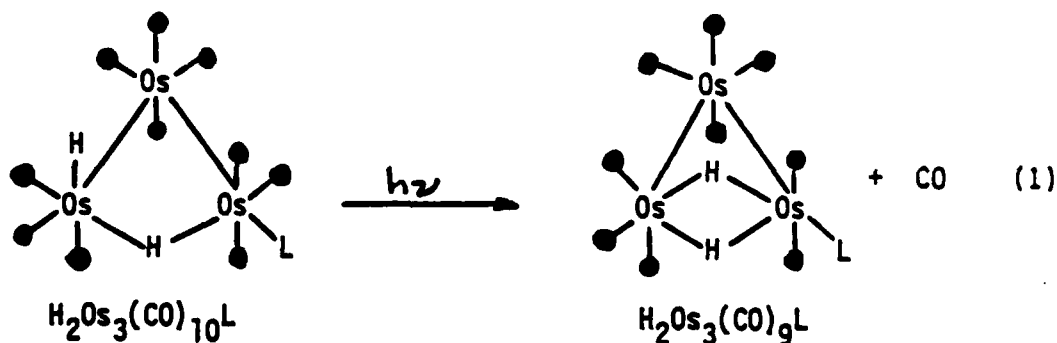
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Abstract

Approx. 100-400 nm  
Near-UV irradiation of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  yields conversion to the known coordinatively unsaturated  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  for  $\text{L} = \text{PPh}_3$  or  $\text{PPh}_2\text{Et}$  in alkane solution at 298 K. Likewise, near-UV irradiation of an alkane suspension of  $[\text{SiO}_2]\text{-L'Os}_3(\text{CO})_{10}\text{H}_2$  yields  $[\text{SiO}_2]\text{-L'Os}_3(\text{CO})_9\text{H}_2$  where  $[\text{SiO}_2]\text{-L'Os}_3(\text{CO})_{10}\text{H}_2$  is the solid prepared by reaction of high surface area  $\text{SiO}_2$  with  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{-}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)$ . The same photochemistry results at 77 K in rigid alkane glasses, but the initial (<5% conversion) product is not derived from loss of CO. Continued irradiation at 77 K yields  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  and CO, but  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  is only found in ~50% yield based on the amount of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  consumed. Warming the irradiated sample to 298 K yields some regeneration of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  and some additional  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$ .

\*Address correspondence to this author.

We wish to report our preliminary results concerning the photochemical generation of reactive intermediates from  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  ( $\text{L} = \text{P-donor}$ ) in solution and on rigid oxide surfaces at 298 and 77 K. Our interest in these systems stems from the fact that the coordinatively unsaturated  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  species are well-characterized<sup>1</sup> and are believed to be important in homogeneous catalytic reactions of olefins.<sup>2</sup> The relative importance of light-induced loss of CO from metal carbonyl clusters compared to metal-metal bond cleavage varies depending on the conditions under which the photochemistry is effected. Light-induced loss of CO from  $\text{Mn}_2(\text{CO})_{10}$ <sup>3</sup> and trans-( $\eta^5\text{-C}_5\text{R}_5$ ) $\text{Fe}_2(\text{CO})_4$  ( $\text{R} = \text{H}, \text{CH}_2\text{C}_6\text{H}_5, \text{CH}_3$ )<sup>4,5</sup> is the dominant photoreaction in rigid media at low temperature whereas net metal-metal bond cleavage dominates in fluid solution at 298 K. Relatively little is known regarding higher nuclearity clusters. The existence of both  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  and  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  complexes, therefore, provides an opportunity to investigate the mechanism of CO loss from these triangular clusters. Thus, the key issues in our study are establishment of (i) whether photoexcitation of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  yields  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  and (ii) the mechanism for the light-induced chemistry. It has been previously established that  $\text{Os}_3(\text{CO})_{12}$  undergoes photosubstitution<sup>6</sup> and that  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\eta^1\text{-SCHN-p-C}_6\text{H}_4\text{F})$  undergoes light-induced loss of CO.<sup>7</sup> Our essential finding is that equation (1) represents the photochemistry at 298 K,



but irradiation at low temperature does not result in CO loss as a primary photoreaction.

We have investigated three systems:  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$ ,  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{Et})$ , and  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2$  prepared from reaction of high surface area  $\text{SiO}_2$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)$ . The molecular species  $\text{H}_2\text{Os}_3(\text{CO})_n\text{L}$  ( $n = 9, 10$ ;  $\text{L} = \text{PPh}_3, \text{PPh}_2\text{Et}, \text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ ) were prepared according to the literature procedures or slight modifications thereof.<sup>1,2,8</sup> The modification of  $\text{SiO}_2$  with  $\text{H}_2\text{Os}_3(\text{CO})_n(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)$  ( $n = 9, 10$ ) was carried out in a manner<sup>9</sup> similar to that previously reported.<sup>10</sup> Characteristic IR and UV-VIS spectral features for the molecular species and modified  $\text{SiO}_2$  are given in Table I.

Near-UV irradiation ( $355 \pm 20$  nm,  $\sim 10^{-6}$  ein/min) of  $\sim 0.5$  mM  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  ( $\text{L} = \text{PPh}_3, \text{PPh}_2\text{Et}$ ) in deoxygenated alkane media at 298 K leads to rapid IR and UV-VIS spectral changes showing that equation (1) represents the photoreaction. The conversion is nearly quantitative up to  $\sim 30\%$  consumption of the starting material when CO is purged from the solution with Ar. The  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  photo-product undergoes slower photoreaction to give unidentified products. Exposure of a solution containing photochemically generated  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  to CO at 1 atm leads to clean regeneration of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ , as expected. Consistent with this finding we note that low extent conversion according to equation (1) is obtained in sealed vessels. The initial 366 nm quantum yield for the photoreaction is  $\sim 0.02$ .

As for  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  in alkane solution, we find that near-UV irradiation of a suspension of  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2$  in deoxygenated alkane initially gives a nearly quantitative yield of  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_9\text{H}_2$ .<sup>11</sup> Again, exposure to CO regenerates the saturated cluster,  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2$ . The irradiation of the  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2$  does not yield detectable cluster in solution. Thus, the



anchoring system is photoinert. The results with  $[\text{SiO}_2]\text{-L'Os}_3(\text{CO})_{10}\text{H}_2$  show that vacant sites on surface-bound clusters can be photogenerated.

Conceptually, the simplest mechanism for the conversion represented by equation (1) for both the homogeneous and suspended saturated cluster is dissociative loss of CO from the photoexcited cluster. However, the CO could originate from any one of the three chemically distinct Os atoms. We have begun an investigation of the mechanism of the photoreaction by monitoring the photochemistry at low temperature in order to trap intermediates.<sup>12</sup> Figures 1 and 2 show the IR spectral changes accompanying the photolysis of the saturated clusters dissolved or suspended in an alkane at -77 K. Note that the IR spectral changes for the surface-bound cluster are very similar to those for the dissolved analogue. Interestingly, the conversion represented by equation (1) appears to occur, as evidenced by the appearance of a feature due to free CO ( $2133\text{ cm}^{-1}$ )<sup>13</sup> and the  $\sim 2092\text{ cm}^{-1}$  band associated with the cluster product shown in equation (1). However, the yield of the unsaturated species and free CO based on consumption of starting cluster increases with the fraction of starting material consumed. The highest yield of the unsaturated cluster is no greater than  $\sim 50\%$  and initially ( $<5\%$  conversion) neither CO nor the cluster product in equation (1) are observed. Figure 3 compares the IR spectral changes upon irradiation of  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  at 298 and 77 K at 8% consumption of starting material. The unsaturated cluster forms cleanly ( $\sim 2092\text{ cm}^{-1}$ ) at 298 K, but none is detected at 77 K. At the lowest extent conversions there is a weak absorption for a product at  $\sim 2128\text{ cm}^{-1}$  (depending on L) that is likely associated with the primary photo-product that does not involve CO loss. As the cluster product in equation (1) forms, CO forms and the ratio of these is constant, but the CO to cluster product ratio is  $\sim 2.0$ .<sup>14</sup> However, the amount of CO formed based on consumption of starting cluster never exceeds a ratio of 1.0. Warm-up of the irradiated sample

to 298 K at the ~2% conversion stage yields regeneration of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  and no detectable  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$ . The product at ~2% conversion is persistent in the dark at 77 K for at least 2 h. Warm-up (to 298 K) of irradiated samples when the  $2092\text{ cm}^{-1}$  band is present yields some additional product and some regeneration of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ ; the  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  account for all Os ( $\pm 10\%$ ) initially present.

The low temperature photochemistry rules out dissociative loss of CO as the primary reaction upon photoexcitation of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ , although  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  is formed as given in equation (1) at 298 K. The fact that more CO than  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  is formed at 77 K indicates the presence of at least one other CO loss product that can back react or give the  $\text{H}_2\text{Os}_3(\text{CO})_9\text{L}$  upon warming to 298 K. Additional studies are underway to establish the structure of the photogenerated intermediates that may derive from a geometrical rearrangement, metal-metal bond cleavage, or loss of hydrogen. Loss of the P-donor is apparently not efficient, since we do not find release of Os species into solution from the irradiation of  $[\text{SiO}_2]\text{-L'Os}_3(\text{CO})_{10}\text{H}_2$ . Interestingly, the low temperature photochemistry of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  departs from the low temperature photochemistry of  $\text{Mn}_2(\text{CO})_{10}^3$  and  $(\eta^5\text{-C}_5\text{R}_5)_2\text{Fe}_2(\text{CO})_4^{4,5}$  that do lose CO upon photoexcitation in rigid media but give metal-metal bond cleavage upon photoexcitation in fluid solution.

Acknowledgements. This research was supported in part by the Office of Naval Research and the National Science Foundation.

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8. Deeming, A.J.; Hasso, S. J. Organomet. Chem., **1975**, 88, C21.
9. High surface area  $\text{SiO}_2$  ( $400 \text{ m}^2/\text{g}$ ) purchased from Alfa was pretreated by heating at  $-250^\circ\text{C}$  under vacuum ( $10^{-2}$  torr) for 48 h. A typical preparation of  $[\text{SiO}_2]\text{-L'O}_3\text{S}_3(\text{CO})_n\text{H}_2$  involves the suspension of  $\sim 1$  g of pretreated  $\text{SiO}_2$  in 100 ml of hexane. The  $\text{H}_2\text{O}_3\text{S}_3(\text{CO})_n\text{L}'$  ( $n = 9, 10$ ,  $\text{L}' = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ ) was added to  $\sim 50 \text{ mM}$  and the suspension stirred at  $25^\circ\text{C}$  for 24 h under  $\text{N}_2$ . Elemental analysis establishes the coverage of cluster to be  $\sim 0.2 \text{ mmol/g}$  or  $\sim 5 \times 10^{-11} \text{ mol/cm}^2$  assuming that the surface area is  $400 \text{ m}^2/\text{g}$ . The solid was collected by filtration and washed repeatedly with hexane, dried under vacuum and under  $\text{N}_2$ . Control experiments using  $\text{H}_2\text{O}_3\text{S}_3(\text{CO})_n(\text{PPh}_2\text{Et})$  ( $n = 9, 10$ ) as the derivatizing reagents yields no surface-confined metal carbonyls after washing with hexane.

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11. UV-VIS photoacoustic spectra of surface-confined materials were taken with a Princeton Applied Research Model 6001 photoacoustic spectrometer. IR spectra were obtained as Nujol mulls.
12. Complexes were dissolved at 298 K to 0.1 - 1.0 mM to insure site-site isolation upon cooling to 77 K. Cooling to 77 K often caused precipitation of these complexes in alkane media. Samples were run at several concentrations to insure that results are not a consequence of aggregation. IR spectra were recorded at 77 K using a Nicolet 7199 FTIR and UV-VIS spectra were recorded using a Cary 17. The Dewar and irradiation procedures have been described previously: Kazlauskas, R.J.; Wrighton, M.S. J. Am. Chem. Soc., 1982, 104, 6005.
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14. The absorptivity of CO in the matrices used is  $\sim 300 \text{ M}^{-1}\text{cm}^{-1}$  based on control experiments involving photodissociation of CO from  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{W}$ ). This allows quantitative determination of the number of CO's lost per molecule. The details of the determination of CO absorptivity will be published elsewhere.

Table I. IR and UV-VIS Data for Relevant Complexes.<sup>a</sup>

Species	Temp, °K	Band Maxima	
		IR cm <sup>-1</sup> (ε or Rel. Abs.)	UV-VIS nm (ε or Rel. Abs.)
H <sub>2</sub> Os <sub>3</sub> (CO) <sub>9</sub> (PPh <sub>3</sub> )	298	2092(5500); 2054(14900); 2012(17800); 2004(4800); 1993(7300); 1976(3400); 1962(1800)	560(200); 357(15800); 302(11700)
	77	2093(8800); 2053(22000); 2015(11000); 2009(24000); 2003(5400); 1993(11000); 1988(6400); 1973(4500); 1961(2500)	355(30000); 307(16000)
H <sub>2</sub> Os <sub>3</sub> (CO) <sub>10</sub> (PPh <sub>3</sub> )	298	2106(2800); 2068(7100); 2052(7900); 2025(15000); 2018(5600); 2008(3600); 2000(3200); 1984(2900); 1972(3000); 1932(290)	388(9800); 333( 0)
	77	2109(3500); 2069(5800); 2051(8500); 2027(17000); 2006(7500); 2000(2600); 1983(2600); 1976(5000); 1955(4400); 1929(510)	375(17000); 325(13000)
H <sub>2</sub> Os <sub>3</sub> (CO) <sub>9</sub> (PPh <sub>2</sub> Et)	298	2092(4300); 2053(11200); 2013(14400); 2005(4400); 1990(5500); 1976(3200); 1957(1900)	352(12800); 297(9800)
	77	2092(6100); 2053(14000); 2011(15000); 2003(2900); 1986(6300); 1973(3900); 1955(3100)	346(21000); 296(14000)
H <sub>2</sub> Os <sub>3</sub> (CO) <sub>10</sub> (PPh <sub>2</sub> Et)	298	2106(2200); 2066(6600); 2051(7800); 2025(14300); 2007(3900); 1999(2900); 1983(2900); 1972(3300)	385(8100); 331(7900)
	77	2107(2200); 2066(7700); 2049(9800); 2030(8900); 2012(9700); 1993(2300); 1988(2300); 1977(4900); 1961(2400); 1929(500)	379(15000); 326(13000)

Table I. (continued)

Species	Temp, °K	Band Maxima	
		IR $\text{cm}^{-1}$ ( $\epsilon$ or Rel. Abs.)	UV-VIS nm ( $\epsilon$ or Rel. Abs.)
$\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{-CH}_2\text{Si}(\text{OEt})_3)$	298	2091(1.00); 2052(2.70); 2012(4.75); 1988(1.74); 1974(0.82); 1954(0.39)	560(1.0); 354(82); 300(67)
$\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}_2\text{-CH}_2\text{Si}(\text{OEt})_3)$	298	2106(1.00); 2066(3.04); 2051(3.55); 2025(7.94); 2007 sh; 1983(1.41); 1972(1.38)	385(1.00); 332(0.96)
$[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_9\text{H}_2^b$	298	2091(1.00); 2052(2.28); 2009(2.82); 1988(1.53); 1953(0.56)	562(1.0); 355(19); 306(20)
$[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2^b$	298	2105(1.00); 2064(3.12); 2048(3.60); 2021(5.46); 1981(1.82); 1968(1.37)	385(1.0); 320(1.1)

<sup>a</sup>All data are for 3-methylpentane solutions, unless noted otherwise.

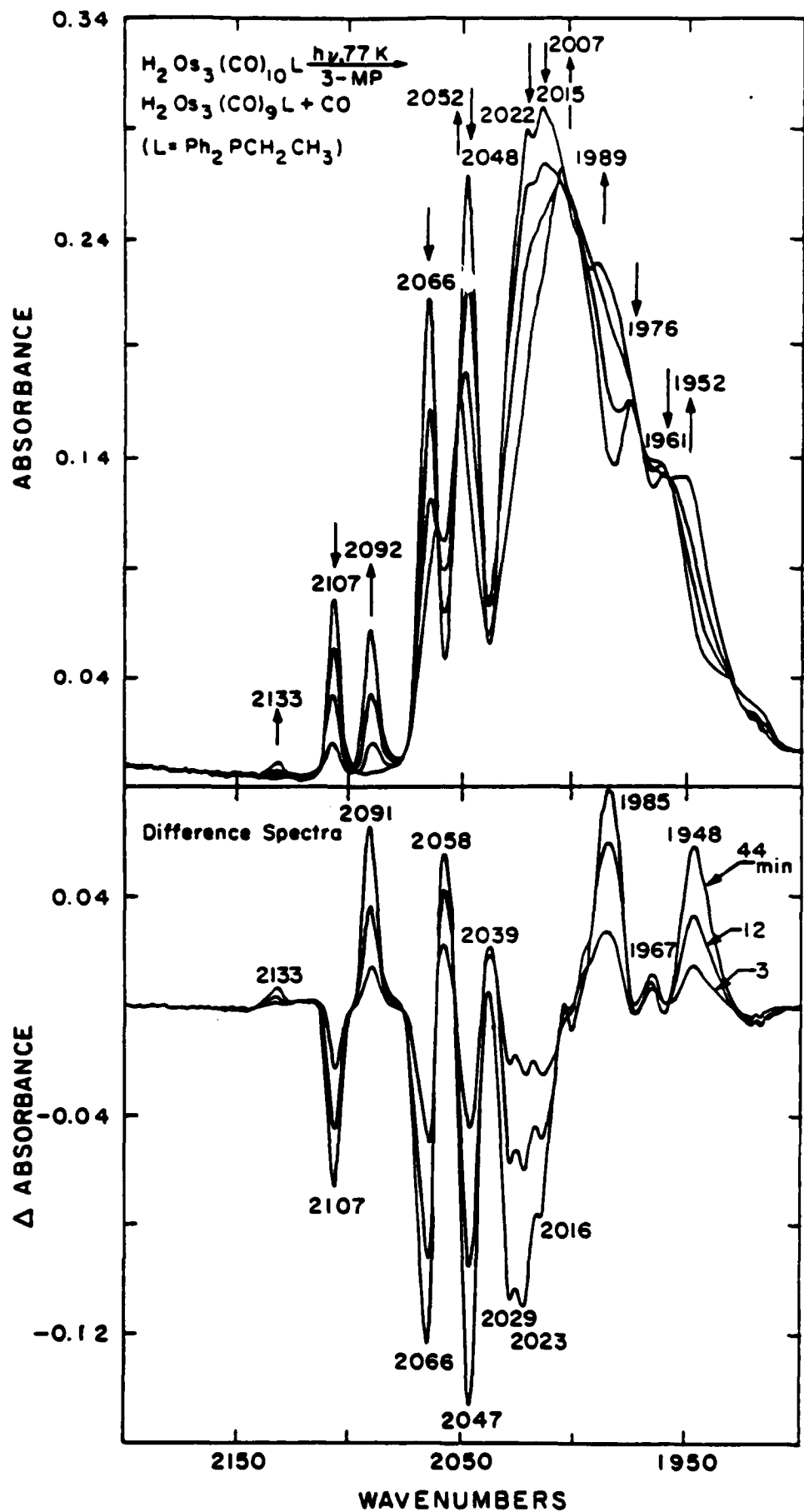
<sup>b</sup>L =  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_{3-n}$ ; n = 1-3. For surface-supported species infrared spectra were recorded as Nujol mulls by FTIR and UV-VIS data were recorded using a photoacoustic spectrometer, PAR 6001.

Figure Captions

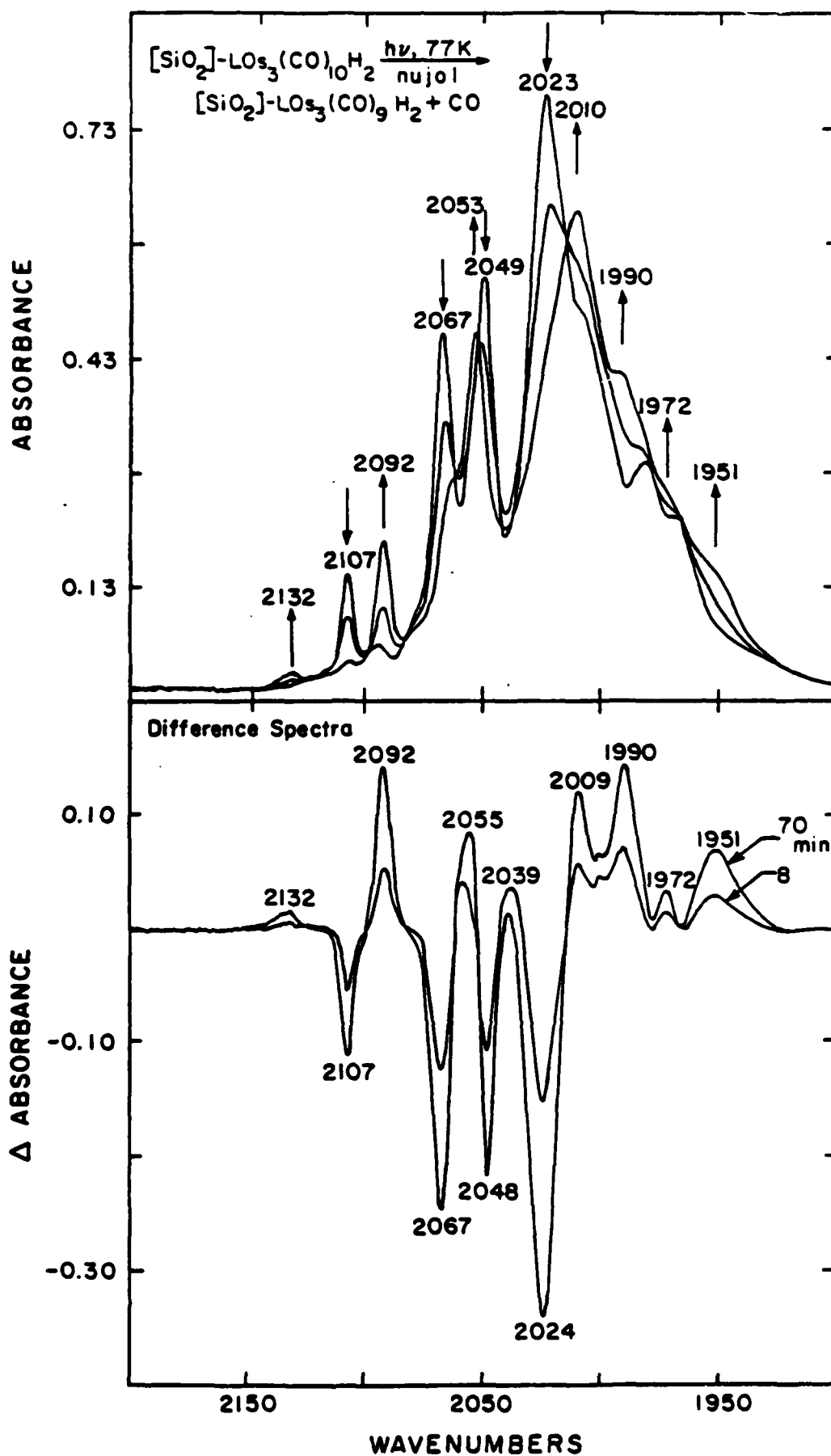
Figure 1. Top: Infrared absorbance changes accompanying near-UV irradiation of  $-1 \text{ mM } \text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{Et})$  in 3-methylpentane at 77 K. Bottom: Infrared difference spectra corresponding to changes shown in top. Positive peaks are product and negative peaks are starting material. Cf. Table I for band positions of starting material and products.

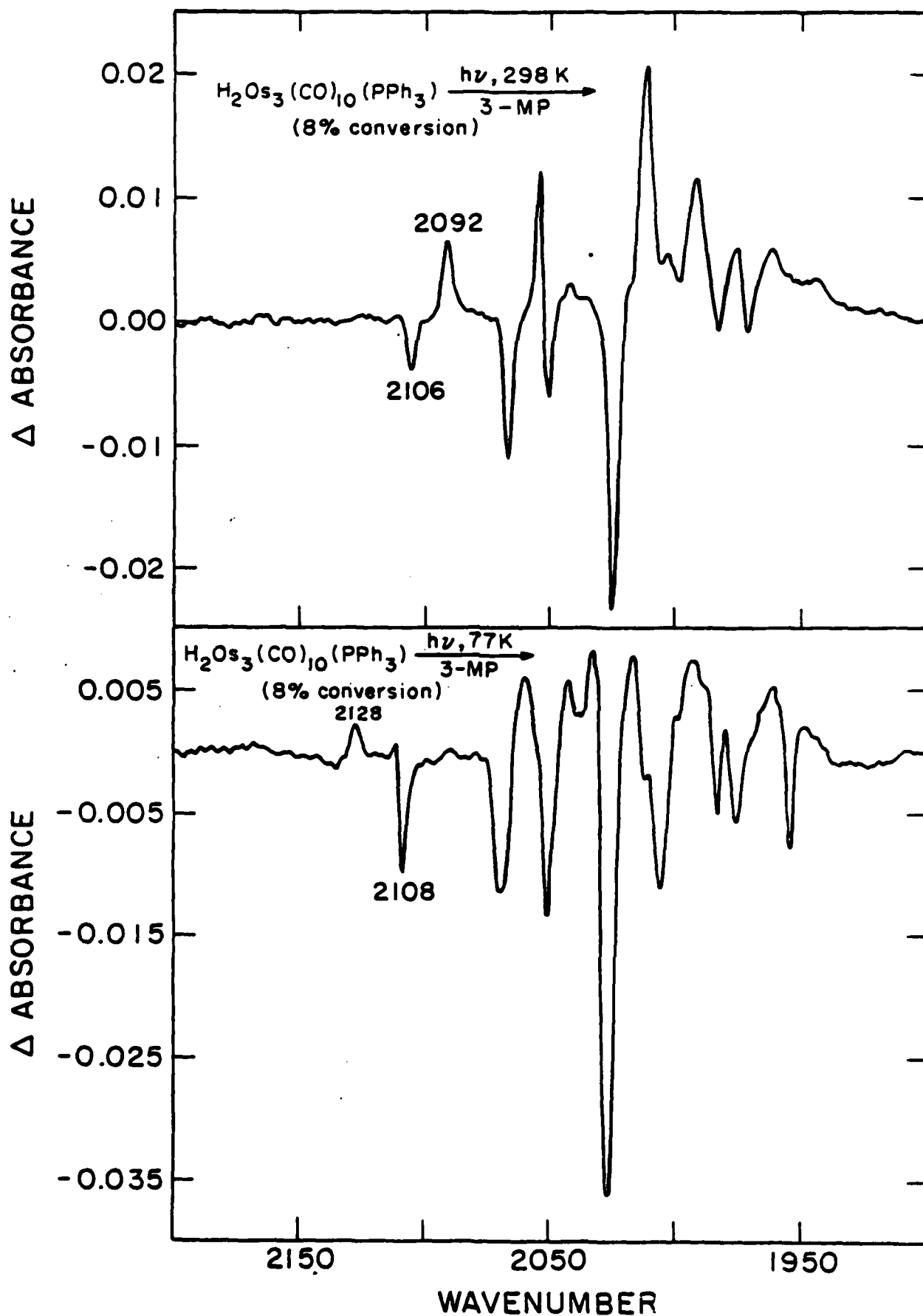
Figure 2. Top: infrared absorbance changes accompanying near-UV irradiation of  $[\text{SiO}_2]\text{-L}'\text{Os}_3(\text{CO})_{10}\text{H}_2$  in a Nujol mull at 77 K. Bottom: infrared difference spectra for the changes shown in the top. Cf. Table I for band positions of starting material and product.

Figure 3. Comparison of difference spectra upon near-UV irradiation at 8% consumption of starting  $1 \text{ mM } \text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  in 3-methylpentane at 298 K and 77 K. Note that at 298 K  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$  is formed ( $2092 \text{ cm}^{-1}$ ) whereas nearly none is detected at 77 K. Further irradiation at 77 K does produce  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$  as for  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$  shown in Figures 1 and 2.









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